

1,150,006



PATENT SPECIFICATION

DRAWINGS ATTACHED

1,150,006

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Int. Cl.:—C 23 c 11/04.

COMPLETE SPECIFICATION

Improvements on or relating to protection coatings for high temperature alloys

We, UNITED AIRCRAFT CORPORATION, a corporation organized and existing under the laws of the State of Delaware, residing at 400 Main Street, East Hartford, Connecticut, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to an improved process for protecting metallic members of dispersion strengthened alloys against oxidation, corrosion and erosion in operation at relatively high temperatures, often above 1200°C. and to product of such a process.

It is an object of the present invention to provide an improved process for providing high-temperature resistant alloys with protective coatings which enable the coated members to withstand exposure to severe environmental conditions at elevated temperatures over relatively long periods of time and coated members formed from dispersion-strengthened alloys which show

improved properties in actual use at elevated temperatures and under severe erosive and corrosive conditions.

It is a proper object of the invention to provide an improved process for the production of gas-turbine blades and vanes and other turbine structures from some of the so-called "dispersion strengthened alloys", such as "TD Nickel", by providing such blades, vanes or structures with a corrosion and erosion-resistant coating so that the good mechanical properties of the TD Nickel or other alloy are retained, at the same time that the surface of the alloy is fully protected against the corrosive and erosive action to which the blades or vanes are subjected in actual use.

Parts, such as blade and vane members for use in gas turbines and to be operated at relatively high temperatures, have heretofore been coated with various protective layers which greatly improve the properties and life of such blades and vanes. However, such coatings of the prior art have proved to be porous or subject to spalling on a dispersion-strengthened metal like TD Nickel

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so that the coatings are not completely protective over long periods of time under severe operating conditions.

According to the present invention, gas-turbine blades and vanes or other parts to be subjected to combustion gases under severe operating conditions of temperature and other factors are formed from an alloy which is adapted to be used at relatively high temperatures, such as are encountered in the operation of modern jet engines and gas turbines and are protected against excessive corrosion and erosion by a multi-layer coating of refractory materials which adhere strongly to the part and protect it against the corrosive and erosive attack of the hot combustion gases which impinge on it.

Many of the dispersion strengthened alloys which have superior mechanical properties at elevated temperatures, such as 1090°C. or higher, are readily susceptible to oxidation, corrosion and erosion under normal operating conditions and therefore cannot successfully be used in their normal condition. Heretofore, it has been suggested that these alloys should be coated with more refractory materials, but the coatings of the prior art, while advantageous, have proved to be unsatisfactory over long periods of severe operation due to the porosity of the coating or its tendency to break away from the underlying surface of the alloy, a condition which is referred to as "spalling".

According to the present invention, a member formed from an alloy selected from the class of dispersion-strengthened nickel-base, cobalt-base and iron-base alloys is first coated with a thin layer of chromium, and then with a thin layer of an aluminium-chromium alloy, the coatings being bonded to each other by diffusion and the underlying chromium coating being diffusion-bonded to the surface of the alloy member. Among the alloys to which the process of the present invention is applicable, and from which the products of the present invention may be formed are alloys such as "TD Nickel" (a duPont alloy consisting by weight of 98% nickel and 2% dispersed thoria), other nickel-base alloys consisting by weight of 20% chromium and 2% thoria, the balance nickels, or 15% molybdenum and 2% thoria, balance nickel, or 20% chromium, 15% molybdenum and 2% thoria, balance nickel; all of which are dispersion-strengthened alloys. In place of thoria, other dispersion strengtheners such as alumina or zirconia, titania, magnesia, hafnia and the rare earth metal oxides may be employed.

Most useful are dispersion-strengthened alloys consisting of nickel, chromium and thoria, nickel, molybdenum and thoria, and nickel, chromium, molybdenum and thoria,

of which the following compositions, by weight, are exemplary:

Nickel	78%	83%	63%
Chromium	20%	—	20%
Molybdenum	—	15%	15%
Thoria	2%	2%	2%

The thicknesses of the chromium layer in the present process may be from $2.54 \cdot 10^{-3}$ to $2.54 \cdot 10^{-2}$ cm preferably from $2.54 \cdot 10^{-3}$ to $12.7 \cdot 10^{-3}$ cm and is formed on the surface of the alloy by packing the cleaned alloy parts in a mass of finely divided mixture composed of chromium metal powder to form the coating and a halogen bearing compound as activator, and a substantially inert filler. Thereafter, the alloy part and the mass of powder are subjected to a diffusion heat treatment, preferably in a hydrogen atmosphere, at a temperature in excess of 982°C. e.g. to 1399°C. and below the melting point of the alloy (1454°C.) for a period of time, such as 15 minutes to 72 hours, preferably about 2 hours at 1316°C. Where the alloy is treated in vacuum the inert filler may be omitted from the pack.

In lieu of packing the blade or vane in a powder mixture, the blade or vane may usually be provided with a coating of chromium by dipping or spraying the blade or vane in an aqueous slurry of the desired chromium powders mixed with a halogen bearing compound, so that the part acquires a coating of such solids, after which it is dried and then subjected to the same heat treatment in vacuum or in an atmosphere which will not react with the materials used as if packed in a powder bed, usually with an inert filler.

Thereafter the alloy part is removed from the powder mixture, any loose particles are removed, and the alloy part is subjected to a second coating process in another powder pack composed of finely divided mixture of aluminium metal powder and chromium metal powder, or a finely divided aluminium/chromium alloy and with an inert filler and a halogen bearing compound as an activator and the part is again subjected to heat treatment in a non-reactive atmosphere, preferably hydrogen, for a period of from 15 minutes to 72 hours, preferably about 2 hours, at a temperature in excess of 538°C. e.g. to 1399°C., preferably about 1149°C. and below the melting point of the alloy. Here also, if the treatment is in a vacuum, the inert filler may be omitted. The treatment is carried out in the absence of deleterious gas to provide the part with an adherant chromium modified substrate-aluminide layer on one chromium layer.

The chromium powder used is preferably finely divided pure chromium metal of particle size 0.149 cm or finer, and it has been found desirable to exclude impurities

such as sulphur and which tend to interfere with the formation of a continuous, adherent coating which is highly resistant to corrosion and erosion at elevated temperatures.

The aluminium powder is also preferably finely divided aluminium metal of particle size 0.149 cm or finer, and relatively pure and substantially free from sulphur and carbon.

The inert powder or filler is generally finely divided alumina, although other inactive powdered materials may be used such as zirconia, titania, ceria, magnesia, hafnia and the rare earth metal oxides.

The activator powder includes a source of halogen such as chromic chloride, bromide, iodide or fluoride, sodium and potassium chloride, potassium fluoride, ammonium chloride, iodide or bromide, in finely divided form, preferably of particle size, 0.149 cm or finer.

While a hydrogen atmosphere is preferred during the heating steps, the heat treatment may be carried out in a vacuum, preferably at an absolute pressure of 1 micron of mercury or less, or in an atmosphere of argon or helium.

Gas turbine blades and vanes, coated in accordance with the present invention exhibit greatly superior corrosion and erosion resistant properties compared with uncoated blades and vanes, as well as compared with blades and vanes coated with chromium alone, or with a duplex coating of chromium

and aluminium alone. Furthermore, blades and vanes coated by the process of the present invention are not subject to catastrophic failure after an extended period of operation, as is characteristic of many of the coated blades and vanes of the prior art.

It will be understood that the foregoing general description and the following detailed description as well are exemplary and not restrictive thereof.

Referring now in detail to the present preferred and illustrative process of the present invention, which will be described in connection with the coating of an otherwise finished vane of a gas turbine adapted to be operated at a temperature of 1200°C. and even as high as 1316°C. The finished vane is preferably formed by forging from "TD Nickel", a dispersion-strengthened alloy composed by weight of 98% nickel and 2% dispersed particles of thoria (ThO₂), the thoria particles being much less than 1 micron in size and substantially uniformly distributed throughout the nickel matrix.

The vane may also be formed by brazing a TDN airfoil member to a platform of TDN or other super-alloy base, such as a nickel-base super-alloy, e.g. IN-100, SM-200, Inconel 713C (Registered Trade Mark), SM-302.

The coating mixture for the first coating to be deposited on the surfaces of the vane comprises a mixture consisting of:

	Range (Weight %)	Preferred Range (Weight gr.)	Optimum (Weight gr.= weight %)
Chromium powder (0.149 cm or finer)	2 to 98%	150 gr.	17.5%=150 gr.
Powdered alumina (Al ₂ O ₃)	2 to 98%	350 to 900 gr.	81.5%=700 gr.
Chromic chloride Anhydrous CrCl ₃	0.1 to 10%	5 to 20 gr.	1.5%= 10 gr.

The optimum mixture is especially suitable for use in vacuum, or in an atmosphere of hydrogen or argon and at temperature of in excess of 982°C. to 1371°C. In general, at higher the temperatures, the chromium content of the pack may be reduced.

These finely divided powders are thoroughly mixed for instance by being blended in a V-blender for a period of 15 minutes or more.

A glass sealed retort to receive the vane is then provided with a substantial layer of the blended powder, usually to a depth of about 2.54 cm, after which the vane is placed in the retort and covered with the blended powder, with all cavities in the vane being filled with the blended powder and areas adjacent the vane are also filled with the blended powder.

The retort is then sealed and is placed in an electrically heated muffle furnace. The muffle is then purged with argon until the oxygen content is substantially nil, after which hydrogen is added to the stream of purging argon. After a few minutes the flow of argon is stopped and the retort and furnace continue to be supplied with hydrogen for the duration of the heat treatment.

The temperature of the furnace is then raised to the diffusing temperature and held in the range of in excess of 982°C. to 1399°C., and below the melting point of the alloy, but preferably at about 1316°C. for a period of time, usually 2 hours or more.

During the heating, the chromic chloride, or other halogen source reacts with the metallic chromium forming a metallic halide,

which decomposes, causing the metallic chromium to be deposited on the surface of the vane as a thin tenaciously adherent layer. The thickness of the deposited chromium layer will vary from $2.54 \cdot 10^{-3}$ cm to $7.62 \cdot 10^{-3}$ cm diffused into the TD nickel to form a solid solution of chromium in nickel, or a combination of solid solutions of chromium in nickel and a solid solution of

nickel in chromium, depending on processing times and temperatures.

Thereafter, the vane is to be provided with a thin adherent layer of chromium modified nickel aluminate, and this is accomplished by treating the vane in a bed of powdered material in a retort. The powdered material comprises a mixture by weight of the following:

		Range	Preferred Range	Optimum
20	Chromium powder (0.149 cm or finer)	2 to 98%	50 to 78%	150 gr.
	Aluminium powder (0.149 cm or finer)	2 to 98%	2 to 50%	30 gr.
	which metal powders are mixed with a mixture of Powdered alumina			
	Chromium Chloride (0.149 cm or finer)	0.2 to 98%		700 gr.
25	to produce a blended mixture.	1 to 10%		10 gr.

The chromium-aluminium is either in the form of blended powders of chromium of aluminium or as a powdered chromium-aluminium alloy. In either case, the chromium/aluminium ratio may vary from 1 to 99% by weight to 99 to 1%, and in the pack, the chromium/aluminium content is preferably from 2 to 98% to 98 to 2% and preferably about 20% of the weight of the total pack.

As the concentration of metal powders in the pack is reduced, for any given temperature, the heat treatment will be extended for those packs including lower amounts of the metal powders.

The vane member is covered with a further layer of the mixed powdered material, and the retort is closed and placed within the electrically heated muffle where it is heated to a temperature in excess of 538°C . to 1399°C ., preferably at 1149°C . for a period of time, preferably about 2 hours, and below the melting point of the alloy of the vane member.

At the start of the heating, the muffle containing the retort is purged with argon, until the oxygen content is substantially nil, after which hydrogen is added to the stream of purging argon. After a few minutes the flow of argon is stopped and hydrogen is supplied for the duration of the heat treatment. After the heating period has been terminated, the flow of hydrogen is continued until the vane has cooled.

There is thus provided a vane which has exceptionally advantageous oxidation and erosion resistant properties as evaluated in a gas turbine operated under test conditions.

In a similar manner, and using the procedures described above, parts formed of other alloys may be provided with a first coating of chromium, and a second coating of aluminium-chromium. The part is then heated in an atmosphere of hydrogen or inert gas, or in a high vacuum, for example

at an absolute pressure of less than 1 micron of mercury, at temperatures in the neighbourhood of 1093°C . or higher for a sufficiently long period of time until the outer chromium-aluminium coating has diffused into the inner chromium coating, thereby providing a chromium-aluminium coating layer which is external to the internal chromium coating layer which is adherent on the vane or other alloy part.

While the chromium layer and chromium-aluminium layers are preferably applied to the metal part by packing the metal part in a powdered mixture of the metals with an inert filler and a halogen bearing compound the coatings may be less advantageously achieved by applying the metal powders to the parts in the form of aqueous slurry, with the halogen bearing compound, which is preferably allowed to dry on the surface of the part prior to heating the slurry-coated part to the temperature required for diffusion of the chromium or chromium-aluminium into the metal part.

Referring to the accompanying drawings:—

Figure 1 is a schematic sectional view of a glass sealed muffle in which a vane is packed for treatment in accordance with the present invention:

Figure 2 is a schematic sectional view, greatly enlarged, of the protective coating applied to the surface of a vane;

Figure 3 is a similar view of a modified form of the coatings applied to a vane;

Figure 4 is a graphical representation of the weight change values obtained by actual test under similar conditions on vanes treated in accordance with the present invention, and on other specimens, with the test temperature at 1149°C .; and

Figure 5 is a graphical representation of the vanes obtained under actual test of erosion at 1204°C . showing the change in weight of a vane member treated according to the

present invention and the member coated according to the best alternative method known to us.

Describing the drawings more in detail:

5 Figure 1 of the drawing shows a retort in which the parts to be coated may be packed for coating. As shown there is provided a pan member 10 in which is seated a retort cap 12 having an open bottom side to rest against the pan member 10. The retort cap member 12 is partially filled in inner retort with pack material 14 while in an inverted position, the vane or other part 16 to be coated placed in the powder, 15 the cap 12 is completely filled with powder and the pan is placed on the open bottom side after which the several parts are inverted to the position shown in Figure 1. The edges around the cap 12 and the rim 20 of the pan 10 are then filled with finely divided glass 18. The retort is then placed in a muffle and is subjected to flowing argon, and then hydrogen for the duration of the heating. The glass particles are of 25 glass which melts below the heat treatment temperature of 982°C. to 1399°C., so that on cooling a seal is provided around the retort, thereby allowing the retort and part 16 to be cooled outside the muffle, while 30 maintaining the part 16 in an atmosphere which will not react with the materials being used. The part 16 may then be removed by breaking the glass seal 18.

Shown in Figure 2 is the body of a part 35 coated in accordance with the present invention where the substrate was chromized at a rate in excess of that at which the chromium diffused into the nickel with the result that a discrete layer of alpha chromium (body centered cubic) was formed over which the aluminium-chromium blend was placed. The body of the part is formed of a dispersion-strengthened super-alloy, such as 40 TD Nickel or other nickel base, cobalt-base or iron base alloy, and is treated according to the present invention first with chromium metal powder and then with a mixture of chromium and aluminium powders. The innermost layer is a solid solution of aluminium and/or chromium in face centered cubic nickel over which is a layer comprising a solid solution of aluminium and/or nickel in body centered cubic chromium. The next 50 outermost layer comprises a face centered cubic solid solution based on Ni₃Al and chromium, and the outermost layer comprises a body centered cubic solid solution based on NiAl and chromium.

The alloy of the part may be an alloy 60 of at least 60% Nickel, from 0.02 to 20% of a dispersed refractory oxide, and the balance, if any, may comprise metals selected from the group of iron, cobalt, aluminium, copper, chromium, molybdenum, 65 tungsten, titanium, tantalum and rhenium.

Figure 3 shows a body of a part coated in accordance with the present invention and in which the chromium was deposited on the substrate at a rate approximately equal to the diffusion rate of the chromium into the 70 nickel with no resultant discrete chromium layer.

In this modification the innermost layer is a solid solution of chromium in nickel, the next layer is a solid solution of 75 aluminium and nickel-chromium. The next outermost layer is Ni₃Al and chromium while the outermost layer is NiAl and chromium.

TD Nickel and related alloys are more 80 fully disclosed in the United States patent specification of Alexander and West, No. 3,180,727 issued April 27, 1965.

As shown in Figure 4, TD Nickel parts treated according to the present invention 85 with a first coating of chromium and a second coating of aluminium-chromium show no substantial gain or loss in weight over long period of operation under simulated engine operating conditions, as plotted 90 on curve A. Test temperature was 1149°C.

Uncoated parts of TD Nickel show a substantial gain in weight which indicates a substantial degree of oxidation resulting in eventual failure, as plotted on curve B. 95

Parts coated with chromium and a second coating of aluminium exhibit a large initial loss in weight, then a gradual loss in weight and an eventual catastrophic failure, as plotted on curve C. 100

Somewhat similarly, parts coated with a thin diffused layer of chromium, show an initially slower rate of erosion, and a more sudden catastrophic failure, as plotted on curve D. 105

Thus, the parts of the present invention remain substantially intact in use, without severe corrosion or erosion or oxidation, and maintain their useful life far beyond the coated parts of the prior art, and are not 110 subject to catastrophic failure.

In Figure 4, weight change in hundredths of a gram is plotted against time in hours.

In another test TD Nickel alloy parts coated in accordance with the present invention were compared with similar uncoated parts of TD Nickel. 115

Figure 5 is a similar group of graphs representing values obtained by actual measurement on TD Nickel parts subjected to oxidation-erosion tests at 1204°C. In this Figure, curves E and F show the weight change in grams plotted against time in hours. Curve E is for a part coated with a composition which is considered by use to be the best of the commercially available intermetallic coatings, while curve F is for a coating comprising an initial chromium and a subsequent outer layer of chromium-aluminium applied according to the process 130

of the present invention.

Two TD Nickel simulated airfoils fabricated from $17,78.10^{-2}$ cm sheet stock with trailing edges welded together were tested, one coated with chromium and aluminium-chromium coatings, the other uncoated, cycled at 35 seconds hot, 25 seconds cold. The thermal shock properties of the coated specimens, i.e., 490 cycles vs. 280 cycles, before failure. The test temperature was 1093°C .

Commercially coated vanes (Vane A) made of high strength cobalt base superalloy in an actual engine configuration were engine tested using turbine inlet temperatures of 1038 and 1093°C against vanes formed from the alloys coated according to the present invention (Vane B), during which tests instrumented vanes adjacent to the vanes under test indicated that temperatures of approximately 126°C were reached in the vane area.

	Turbine Inlet Temp.		Total Time
	1038°C .	1093°C .	
vane A	71.49 hrs.	40.39 hrs.	139.111 hrs.
vane B	89.69 hrs.	50.76 hrs.	137.49 hrs.

After the vane or blade member has been treated according to the present invention it has an exterior layer of aluminium-chromium superimposed on a layer of nickel-chromium-aluminium alloy, which in turn is bonded to the base metal by a layer of nickel-aluminium-chromium. The commercially coated superalloy vanes had to be air cooled to endure these temperatures; however the cooled TD Nickel vanes endured those higher metal temperatures without air cooling.

WHAT WE CLAIM IS:—

1. A method of protecting metal alloy pieces against oxidation, corrosion and erosion at relatively high operating temperature in excess of 982°C and below the gases, comprising contacting intimately a part formed from an alloy selected from the class consisting of the nickel-base, cobalt-base and iron-base, high-temperature resistant alloys with a finely divided mixture comprising chromium powder and a halogen-bearing compound, characterized in that the coated part after being heated at a temperature in excess of 982°C and below the melting point of the alloy, in the absence of deleterious gas to provide the part with an adherent layer of chromium, is contacted with a finely divided powder comprising aluminium and chromium metals mixed or alloyed and a halogen-bearing compound to be heated thereafter at a temperature in excess of 538°C and below the melting point of the alloy, and in the absence of deleterious gas to provide the part with an adherent chromium-modified substrate-aluminide layer on the chromium layer

which is adherent on the alloy part.

2. The method according to claim 1, characterized in that the alloy part is formed of an alloy consisting of at least 60% nickel, from 0.02 to 20% of a dispersed refractory oxide and that the balance, if any, of the alloy comprises metals selected from the group consisting of iron, cobalt, aluminium, copper, chromium, molybdenum, tungsten, titanium, tantalum and rhenium.

3. The method according to claim 2, characterized by using an alloy which is a dispersion-strengthened alloy.

4. The method according to either claim 2 or 3, characterized by selecting the dispersed refractory oxide from the group consisting of thoria, alumina, zirconia, titania, magnesia, hafnia and the rare earth metal oxides.

5. The method according to any one of claims 1-4, characterized by using a dispersion-strengthened nickel-base alloy containing 20% chromium and 2% thoria, balance nickel.

6. The method according to any one of claims 1-4, characterized by using a dispersion strengthened nickel-base alloy containing 15% molybdenum and 2% thoria, balance nickel.

7. The method according to any one of claims 1-4, characterized by using a dispersion strengthened nickel-base alloy containing 20% chromium, 15% molybdenum and 2% thoria, balance nickel.

8. A metal article resistant against oxidation, corrosion and erosion at relatively high operating temperatures while subjected to combustion gases comprising a base alloy selected from the class consisting of the nickel-base, cobalt-base and iron-base, high temperature resistant alloys and prepared according to the method of any one of claims 1-7, characterized in that the article is enclosed within a diffusion coating which comprises an inner layer containing chromium and an outer layer containing an aluminium-chromium alloy adapted to be exposed to the combustion gases.

9. The metal article according to claim 8, characterized in that the base alloy consists of at least 60% nickel, and the outer layer of the coating consists of chromium-modified nickel-aluminide.

10. The metal article according to claim 8 or 9, characterized in that the chromium layer has a thickness from $2.45.10^{-3}$ cm to $2.54.10^{-2}$ cm.

11. A metal article according to any one of claims 8-10, characterized in that the article is a gas turbine blade.

12. A metal article according to any one of claims 8-10, characterized in that the article is a gas turbine vane.

13. A metal article according to any one of claims 8-12, characterized in that the

- coating consists of an innermost layer of a solid solution of aluminium and/or chromium in face centered cubic nickel, a first intermediate layer comprising a solid solution of selected aluminium and/or nickel in body centered cubic chromium, a second intermediate layer comprising a face centered cubic solid solution of Ni_3Al and chromium, and an outermost layer comprising a body centered cubic solid solution of NiAl and chromium, the layers of the coating being bonded to each other by diffusion and the innermost layer being diffusion-bonded to the base alloy.
14. A metal article according to any one of the claims 8-12, characterized in that the coating consists of an innermost layer of solid solution of chromium in nickel, a first intermediate layer of a solution of aluminium and nickel-chromium, a second intermediate layer of Ni_3Al and chromium, and an outermost layer of NiAl and chromium, the layers of the coating being bonded to each other by diffusion and the innermost layer being diffusion-bonded to said alloy.
15. A metal article according to any one of the claims 8-14, characterized in that the coating has an inner diffusion layer of chromium adherent to the base alloy formed by diffusing a chromium powder on the base

alloy, and an outer diffusion layer formed by diffusing a mixture of aluminium and chromium powders on the inner layer consisting of from 2 to 98% by weight aluminium and the balance chromium.

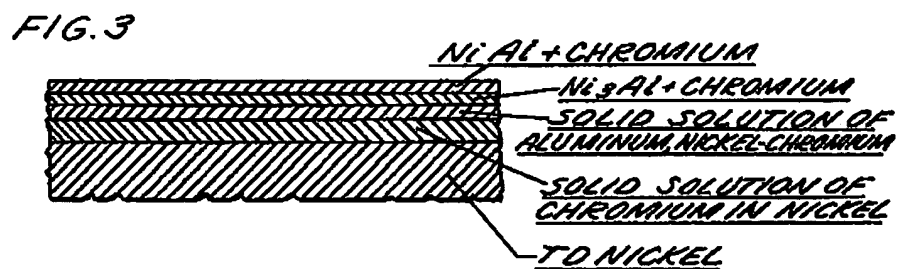
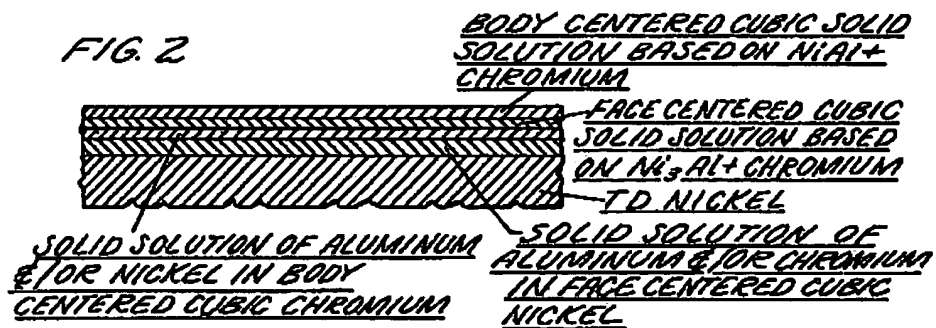
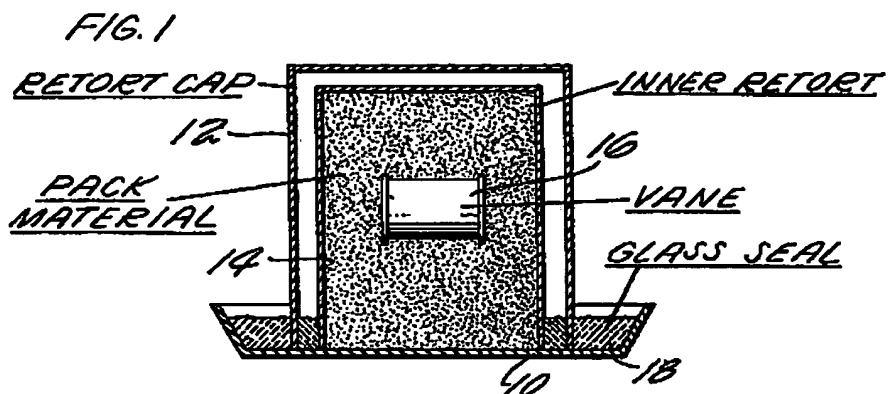
16. A metal article according to claim 15, characterized in that the mixture of aluminium and chromium consists by weight of from 2 to 50% by weight aluminium and the balance chromium.

17. A metal article according to claim 10, characterized in that the chromium layer is from $2.54 \cdot 10^{-3}$ cm to $12.7 \cdot 10^{-3}$ cm thick.

18. A method of protecting metal alloy pieces against oxidation, corrosion and erosion at relatively high temperatures, the method being according to claim 1 and substantially as described in the examples.

19. Metal alloy pieces whenever treated by the method claimed in any one of claims 1 to 7.

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1,150,006

2 SHEETS

COMPLETE SPECIFICATION

This drawing is a reproduction of the Original on a reduced scale.

SHEETS 1 & 2

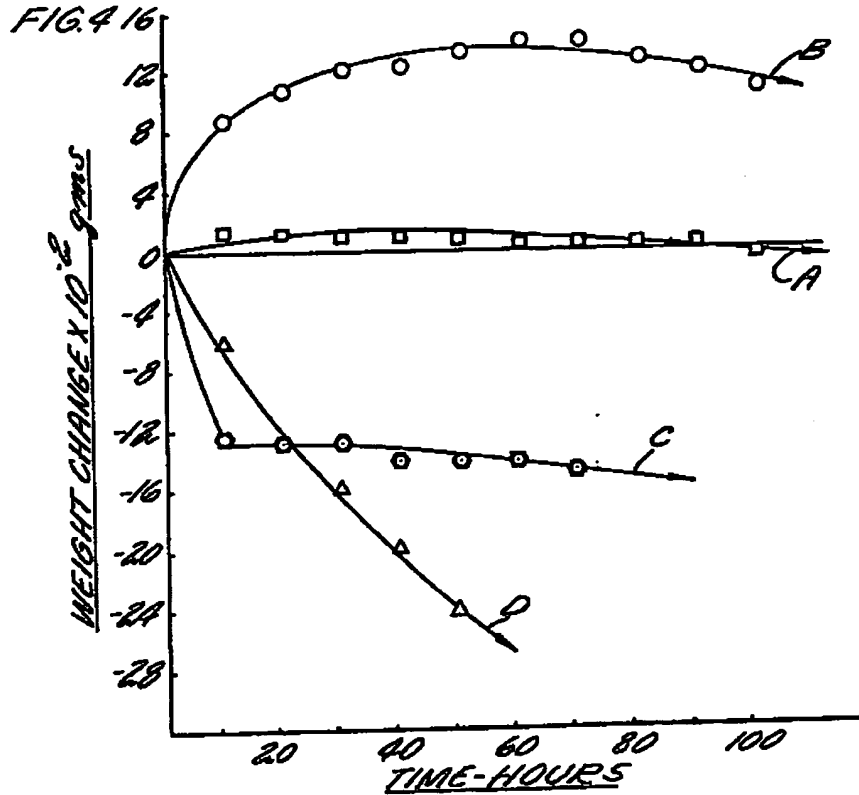


FIG. 5

